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FROM NANOCLUSTERS TO CLIMATE FORCERS: GLOBAL MODELING OF AEROSOL CLIMATE EFFECTS

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Academic dissertation

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Risto Juhani Makkonen
University of Helsinki, 2012

Abstract

Atmospheric aerosol particles influence everyday life through their adverse health effects. Aerosols also affect the Earth's climate, directly by scattering and absorbing radiation and indirectly by acting as cloud condensation nuclei (CCN) and modifying cloud properties. The net effect of aerosols on climate is cooling. Although only a small fraction of atmospheric aerosol mass is of direct human origin, the anthropogenic aerosol climate forcing can be of same magnitude, but opposite in sign, as the anthropogenic forcing via CO_2. As aerosols are short-lived and respond rapidly to changes in emissions, they are an important factor in determining the future climate change.

Aerosols are either emitted as primary particles or they are formed from gas-phase precursors. Atmospheric new particle formation is observed around the world. In this thesis, new particle formation is studied with a global aerosol-climate model. Several thermodynamic and semi-empirical parameterizations of nucleation are investigated. It is shown that in addition to the thermodynamic models, semi-empirical parameterizations are needed to explain the observed aerosol number concentrations.

Volatile organic compounds (VOCs) can contribute to particle number, particle growth, and total aerosol mass. It was shown that biogenic VOCs have an important role in growing the freshly-nucleated particles to sizes capable of acting as CCN.

It was also shown that the current atmospheric concentrations of nitric acid can greatly affect cloud droplet activation and increase the number of cloud droplets, making a large contribution to the indirect aerosols effect.

With current scenarios for anthropogenic SO_2 emissions, the formation of new particles will diminish significantly by the year 2100. Together with the predicted reductions in primary particles, the future cloud droplet number concentrations were shown to decrease close to pre-industrial levels. As a result, the anthropogenic aerosol forcing decreased close to zero. Several possible counteracting processes were studied. It was shown that an increase in either oceanic dimethyl sulfide (DMS) or biogenic VOC emission could provide more CCN and cooling in the future. Also, the differences in the predicted future trend of NO_x and SO_2 emissions indicate an increasingly important role for the indirect effects via nitric acid.

Keywords: atmospheric aerosols, nucleation, BVOC, climate, global model

Contents

List of publications

This thesis consists of an introductory review, followed by 4 research articles. In the introductory part, these papers are cited according to their roman numerals. Papers are reprinted under the Creative Commons License.

I Makkonen, R., Asmi, A., Korhonen, H., Kokkola, H., Järvenoja, S., Räisänen, P., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., Järvinen, H., Lohmann, U., Bennartz, R., Feichter, J., and Kulmala, M. (2009). Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5-HAM global circulation model. *Atmos. Chem. Phys.*, 9:1747–1766.

II Makkonen, R., Asmi, A., Kerminen, V.-M., Boy, M., Arneth, A., Hari, P., and Kulmala, M. (2012). Air pollution control and decreasing new particle formation lead to strong climate warming. *Atmos. Chem. Phys.*, 12:1515-1524.

III Makkonen, R., Asmi, A., Kerminen, V.-M., Boy, M., Arneth, A., Guenther, A., and Kulmala, M. (2012). BVOC-aerosol-climate interactions in the global aerosol-climate model ECHAM5.5-HAM2, *Atmos. Chem. Phys. Discuss.*, 12:9195-9246.

IV Makkonen, R., Romakkaniemi, S., Kokkola, H., Stier, P., Räisänen, P., Rast, S., Feichter, J., Kulmala, M., and Laaksonen, A. (2012). Brightening of the global cloud field by nitric acid and the associated radiative forcing, *Atmos. Chem. Phys. Discuss.*, 12:5225-5245.

1 Introduction

Atmospheric aerosols affect the everyday life on Earth. Vast amounts of tiny particles, ranging in size from nanometers to hundreds of micrometers, are entering the atmosphere from natural and anthropogenic sources. While in the atmosphere, aerosol particles can affect radiative fluxes, chemical processes and cloud microphysics. When leaving the atmosphere, the aerosols can have several positive and negative effects.

Airborne aerosol particles can enter the pulmonary system, and depending on the aerosol composition, cause severe medical conditions (Seaton et al., 1995). World Health Organization has estimated that globally, about 725 000 life-years are lost due to exposure to aerosols, especially to those produced by combustion (WHO, 2003). Recent studies have linked even several hundred thousands losses of human life to landscape fire smoke (Johnston et al., 2012), and ship-emitted particles alone could be responsible for 60 000 deaths annually (Corbett et al., 2007).

Besides the negative impacts on human health, aerosols have a strong influence on the atmospheric radiative fluxes. The airborne particles scatter and absorb radiation (Karl et al., 1986). Backscattering of thermal radiation from large dust particles makes a small contribution to the greenhouse effect, but more importantly, aerosols absorb and scatter solar radiation. Aerosols can also affect the properties of clouds, since each cloud droplet in the atmosphere is formed on an existing aerosol particle. The optical and microphysical properties of the cloud are largely determined by the amount of available aerosol number concentration. The understanding of the aerosol-cloud coupling is still poor (Forster et al., 2007).

Aerosol particles can be emitted to the atmosphere as primary particles, for example as sea salt crystals from oceans (Jaeglé et al., 2011), mineral dust from deserts (Huneeus et al., 2011), or primary biological particles from vegetation (Després et al., 2012). Gaseous compounds can undergo gas-to-particle conversion in the atmosphere, forming secondary aerosols. The formation of new particles from gaseous precursors has been observed around the world (Kulmala et al., 2004b). The freshly-formed particles are of nanometer-size, and not of direct climatic importance. However, with a sufficient amount of condensing vapours available, these particles can grow to sizes where they can affect cloud properties (Kerminen et al., 2005). Organic vapours, especially of biogenic origin, can be of major importance with regards to particle growth.

The aerosol effects on climate are a crucial factor in the future evolution of climate change. If the present-day aerosol effects are small, also the climate sensitivity, and thereby the future temperature change, are expected to be small (Andreae et al., 2005). However, with a strong present-day aerosol forcing, the climate could be very sensitive to the imposed greenhouse gas emissions.

With the environmental and health issues in mind, legislations and directives have been regulating particulate emissions for decades. While some controversy exists for the predicted evolution of particulate emissions during the first half of the 21st century, all future scenarios agree that most aerosol and precursor emissions will be decreased, even to a large extent, from the present-day levels until the end of the 21st century (Forster et al., 2007; Lamarque et al., 2011). As a result, if the present-day anthropogenic aerosol effect is strong, a significant reduction in the aerosol emissions could lead to a loss in the cooling effect of aerosols. To assess the evolution of climate requires quantification of the present-day aerosol effect, understanding the governing processes and mechanisms, and depicting scenarios of anthropogenic and natural emissions of aerosols and their precursors.

The goal of this thesis is to investigate the role of new particle formation, secondary organic aerosols and soluble trace gases on climate. More specifically, this thesis aims to address the following questions

-To what extent can new particle formation increase the number concentration of cloud droplets?

-What is the role of biogenic organic vapours on aerosol particle number concentrations, especially for the growth of nucleated particles?

-How much can nitric acid affect cloud droplet activation?

-What is the contribution of these processes on the present-day aerosol forcing, and how does the aerosol forcing change by the year 2100?

-What is the role of climate feedbacks by BVOC and DMS in the warming climate?

2 Global aerosol-climate model ECHAM5-HAM

The work in this thesis is based on computational simulations with the global aerosol-climate model ECHAM5-HAM (Stier et al., 2005), which is a combination of the aerosol module HAM (Hamburg Aerosol Model) and the host-model, general circulation model ECHAM5 (Roeckner et al., 2003).

The ECHAM5 and HAM are only a subset of models that can be integrated into larger ensembles, ultimately into an Earth System Model (ESM). The ECHAM5 can be run with fixed sea-surface properties (temperature and ice cover), a mixed-layer ocean model, or a full ocean model MPIOM (Marsland et al., 2003). Additionally, for example the land vegetation model JSBACH or ocean biogeochemistry model HAMOCC can be coupled to ECHAM5.

In this thesis, **Papers I and II** use the model version ECHAM5-HAM (Stier et al., 2005) with the cloud microphysics described in Lohmann et al. (2007). The **Papers III and IV** use the second generation of the aerosol module, ECHAM5.5-HAM2, which is described in Zhang et al. (2012).

The spectral resolution of T42 has been used in all simulations in this thesis. This corresponds to a grid of 128x64 (lon x lat), and about 2.8°x2.8° or 300 km grid spacing at the Equator. Although the selected grid size is rather coarse for comparisons with site observations, the computational burden is low enough to allow for sensitivity studies. The simulations in **Paper I** used 19 vertical levels, while **Papers II, III and IV** used 31 levels to better capture the vertical distribution of aerosols. The ECHAM5 uses hybrid-sigma vertical coordinate system, which allows for terrain-following levels near surface (sigma-levels) and pressure-levels in the upper troposphere and stratosphere. In the standard version of ECHAM5 used in this thesis, the highest level is at 10 hPa.

2.1 Aerosol microphysical model M7

The aerosol size distribution has to be discretized for modeling purposes. In regional and global aerosol models, this is usually achieved by dividing the aerosol size spectrum into bins or modes (Kukkonen et al., 2012). The amount of bins or modes varies from 2 to several tens (Textor et al., 2006).

The aerosol microphysical model inside ECHAM5-HAM is M7 (Vignati et al., 2004). The M7 model takes a modal approach to describe the aerosol size distribution. Aerosol mixing state is described by dividing the modes into three insoluble (no or low water-solubility) and four soluble modes. The soluble modes cover the size range with nucleation (number mean radius $\bar{r}$ <5 nm), Aitken (5 nm< $\bar{r}$ <50 nm), accumulation (50 nm< $\bar{r}$ <500 nm) and coarse ($\bar{r}$ >500 nm) modes. The nucleation mode is omitted from the insoluble aerosol distribution. All modes are assumed to be log-normal:

$$n(ln\ r) = \sum_{i=1}^{7} \frac{N_i}{\sqrt{2\pi} ln\ \sigma_i} exp\left(-\frac{(ln\ r - ln\ \bar{r}_i)^2}{2ln^2\ \sigma_i}\right), \quad (1)$$

where N_i is the concentration and σ_i is the standard deviation of mode i. The coarse modes are assumed to have a standard deviation σ of 2.00, while the smaller modes are narrower with a standard deviation of 1.59.

To save computational resources, not all compounds are included in all modes. Sea salt is included only in the soluble accumulation and coarse modes. Freshly-emitted dust is assumed to be insoluble, but condensation of sulfate can convert dust particles to soluble. Dust is therefore included in both soluble and insoluble accumulation and coarse modes. Emissions of organic and black carbon are often coincident, and both compounds are modeled in the insoluble Aitken mode and all soluble modes except nucleation mode. In this work, organic carbon tracer is included in each mode. Finally, sulfate is assumed to exist in all modes, however it is only traced in the soluble modes. One monolayer of sulfate condensed on insoluble particles converts them to water-soluble, and those particles (together with the condensed sulfate) are moved to the corresponding soluble modes.

Although there are computational benefits of covering the aerosol size distribution with only four modes, the modal setup is not optimal with regard to individual aerosol dynamical processes. Any mode has to keep track of existing particles in the mode, and somehow deal with particles entering the mode via condensational growth or nucleation. If nucleation occurs intermittently, the nucleated particles might be able to grow to the Aitken mode before the next nucleation burst. For the Aitken mode, the situation is further complicated by the primary particle emissions, which are applied at each timestep. Hence, the Aitken mode must follow the growth of both particles grown from the nucleation mode, and freshly emitted primary particles ($\bar{r}$ ∼30 nm). The dynamics

of the Aitken mode are crucial for cloud droplet activation, since the activation radii of cloud droplets is usually located in the larger end of the Aitken mode.

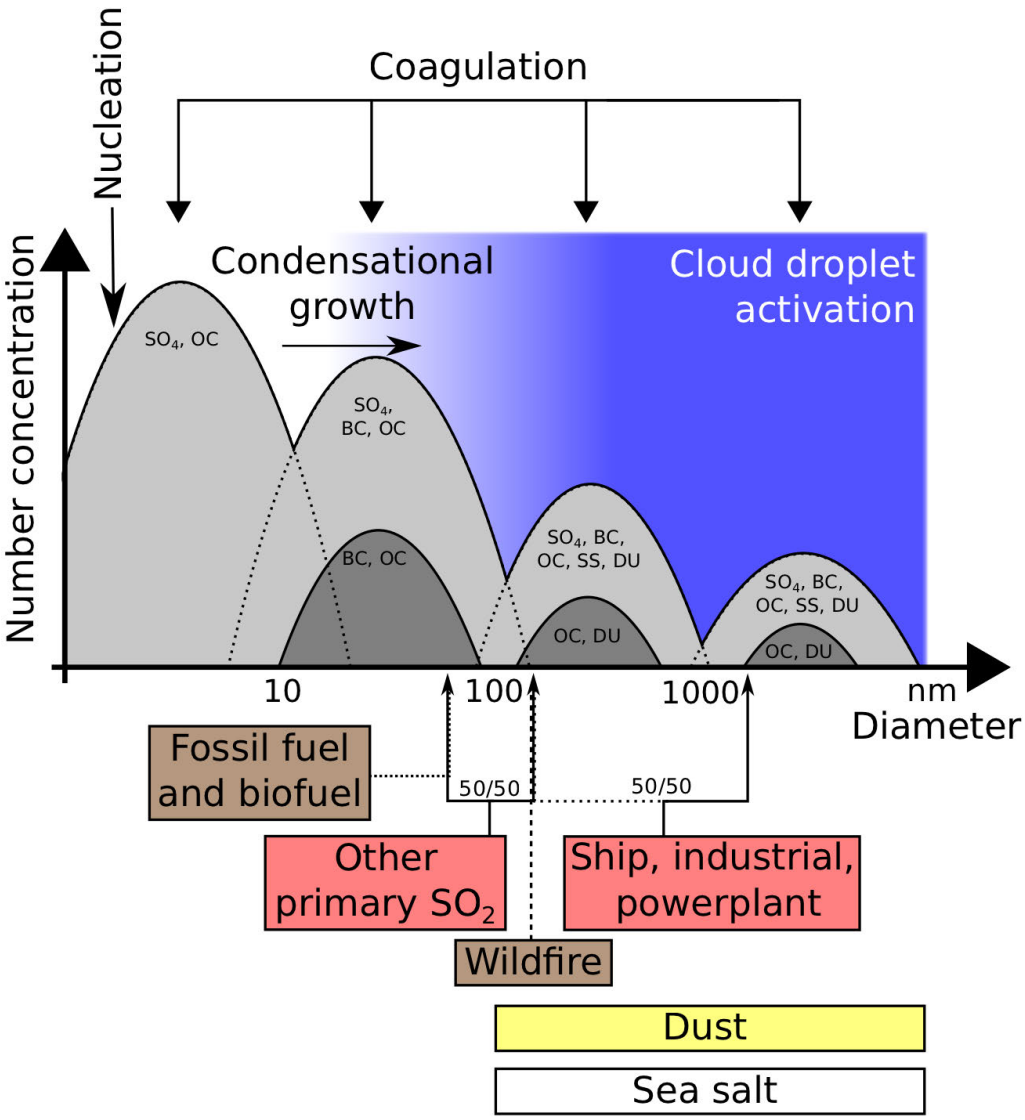

Figure 1: The modal setup of the M7 aerosol module, showing also the prescribed sizes of anthropogenic primary emissions (brown=OC+BC, red=sulfate) and the ranges of dust (yellow) and sea salt (white) emissions. Primary sulfate refers to the fraction of SO_2 emission that is assumed to convert to aerosol mass during one timestep. Sulfuric acid and organic vapours can condense on each mode.

Figure 1 shows the modal setup of M7 together with the size ranges of primary emissions. The blue area corresponds to the size range that is relevant for cloud droplet

activation. Many primary particles, for example from wildfire emissions, are already at or close to the sizes relevant for cloud droplet activation ($\bar{r}$ >35 nm).

3 New particle formation

3.1 The nucleation process

The process of atmospheric new particle formation involves two important steps (Kulmala and Kerminen, 2008). First, a cluster of critical size must be formed via nucleation. Second, there must be vapours to condense on the cluster and provide growth. In general, nucleation is the starting point of a phase-change. In atmospheric nucleation, vapours of low volatility form solid or liquid clusters. The process can be either heterogeneous (vapour molecules attaching on an existing surface) or homogeneous (vapour molecules have to create a surface for the cluster). Since the creation of the surface requires energy, heterogeneous nucleation is easier and more frequent in atmosphere, where pre-existing surfaces are usually available.

Even if vapour molecules collide to form a cluster, there might be excessive energy involved which leads to breaking of the cluster soon after. Hence, the cluster would need an additional component to remove the excess energy and stabilize the cluster.

After the aerosol particle has nucleated, i.e. reached the critical size, vapours of low volatility will condense on the particle surface. The faster the growth, the better chance of survival of the particle, since nanometer-sized particles are easily lost by coagulation (Kerminen et al., 2004; Pierce and Adams, 2007). The vapours responsible for the nucleation and further growth don't necessarily need to be the same, and these two processes can be uncoupled in the atmosphere (Kulmala et al., 2000a).

3.2 Atmospheric observations

Observation of new particle formation requires instruments able to detect particles of <20 nm in diameter, and preferably even smaller particles of 1–3 nm. Measurements of atmospheric nucleation-mode particles have been made already in the 1990s, with the first measurements focusing on the marine boundary layer (Covert et al., 1992; Hoppel

et al., 1994; Van Dingenen et al., 1995; Weber et al., 1995; Wiedensohler et al., 1996) and free troposphere (Clarke, 1992; Hofmann, 1993). A while later, nucleation was found also in the continental boundary layer (Aalto et al., 1995; Marti et al., 1997). Around this time it was also observed that, in contrast to the marine boundary layer, the nucleated particles in the boreal forest grow to Aitken-mode size during 6-12 hours (Mäkelä et al., 1997).

To date, new particle formation has been observed around the world (Kulmala et al., 2004b; Kerminen et al., 2010). New particle formation is observed in polluted Beijing (Wang et al., 2011), as well as in remote marine (Ehn et al., 2010), coastal (Modini et al., 2009) and continental sites (Asmi et al., 2011). Observations have been done in the warm tropics (Clarke et al., 1998) as well as in the cold upper troposphere and lower stratosphere (Lee et al., 2003). Only in Amazon, new particle formation has not been routinely observed (Kanawade et al., 2011).

3.3 Possible compounds involved

Sulfuric acid is suggested as the principle compound in atmospheric nucleation (Weber et al., 1995; Kirkby et al., 2011). Ammonia can stabilize the sulfuric acid-water clusters, leading to decreased critical cluster sizes and increased nucleation rates (Weber et al., 1998; Korhonen et al., 1999; Kulmala et al., 2000b). In highly polluted regions, gas-phase ammonia could be limiting new particle formation (Gaydos et al., 2005). In some coastal locations, iodine compounds could be responsible for nucleation (O'Dowd et al., 2002).

Recent calculations have shown that amines can enhance sulfuric acid nucleation rates more effectively than ammonia (Loukonen et al., 2010). The sulfuric acid-amine nucleation has since been observed in laboratory (Erupe et al., 2011; Yu et al., 2012b) and atmosphere (Zhao et al., 2011). Amine sources (285±78 Gg(N)/yr for methylamines) have been estimated far smaller than those for ammonia (50000±30000 Gg(N)/yr) (Ge et al., 2011), however, there are still large uncertainties involved in the emission sources.

3.4 Role of ions

Ions, originating from cosmic rays, radon decay and gamma radiation (Israel, 1970; Bazilevskaya et al., 2008), are ubiquitous in the atmosphere (Hirsikko et al., 2011). Electrostatic effects can greatly enhance molecular collisions and lead to increased nucleation rates (Yu and Turco, 2000). While ion-induced nucleation has been suggested to be a major contributor to atmospheric new particle formation (Yu et al., 2010), several observations have indicated only a small contribution from ion-induced nucleation (Eisele et al., 2006; Kulmala et al., 2007; Hirsikko et al., 2011), and no link has been observed between the solar cycle (cosmic ray intensity) and new particle formation (Kulmala et al., 2010).

3.5 Parameterizations of nucleation

The classical nucleation theory (CNT) describes the formation of a spherical cluster or droplet, using macrophysical properties to describe the thermodynamics of the cluster. However, atmospheric nucleation rates are too high to be explained by thermodynamic nucleation of sulfuric acid and water (Weber et al., 1996). CNT with sulfuric acid, ammonia and water might even overestimate nucleation rates (Lucas and Akimoto, 2006). For modeling purposes, results from CNT have been parameterized for both sulfuric acid-water nucleation (Kulmala et al., 1998; Vehkamäki et al., 2002) and sulfuric acid-ammonia-water nucleation (Napari et al., 2002; Merikanto et al., 2007).

As the classical thermodynamical models of nucleation have failed to explain atmospheric observations, alternative approaches have been developed for modeling purposes. Large datasets of simultaneous measurements of nucleation rate, growth rate, sulfuric acid concentration and meteorological variables give the opportunity to parameterize the particle formation rates. Measurements of atmospheric sulfuric acid concentration are still rather sparse, but campaign-wise data have been increasingly available in the recent years.

First semi-empirical parameterizations of atmospheric new particle formation rate were introduced in 2006, based on a measurement campaign in 2003 in Hyytiälä, Finland (Kulmala et al., 2006; Sihto et al., 2006). During the campaign, the nucleation rate seemed to correlate with the sulfuric acid concentration to the power between one and two. The sulfuric acid dependence of the nucleation rate was therefore significantly

lower than what is predicted by classical models. The exponent of one can be explained by the activation mechanism, according to which neutral or ion clusters are activated for further growth, if they contain one sulfuric acid molecule (Kulmala et al., 2006). The exponent of two would suggest kinetic nucleation or sulfuric acid (McMurry and Friedlander, 1979).

Recently, the increase in atmospheric measurements of sulfuric acid concentrations and aerosol size distributions has established basis for several new parameterizations for new particle formation. Riipinen et al. (2007) continued the work of Sihto et al. (2006) by extending the analysis over new campaigns in Hyytiälä and Heidelberg. Again, a power law relation with exponents ranging from 1 to 2 was found between sulfuric acid concentration and particle formation rate at 3 nm. In Paasonen et al. (2010), particle formation events from four European sites were analyzed, and several formulations of nucleation were tested against the data. Including organic vapours in the nucleation parameterization seems to improve correlation with observations (Paasonen et al., 2010). Empirical parameterizations for ion-induced nucleation are also available (Nieminen et al., 2011).

3.6 Modeling new particle formation in a global scale

The need for reliable models for nucleation in climate models was underlined in Kulmala et al. (2004b). With the evolution of the aerosol microphysical representation in global models, it became obvious that the modeled aerosol number concentrations were systematically lower than observed, especially in the boundary layer (Stier et al., 2005; Spracklen et al., 2005). While the discrepancy could arise from several sink and source processes, it was also known that the representation of nucleation, generally based on CNT, was inadequate. During the last 6 years, several global models have been successfully complemented with semi-empirical aerosol nucleation formulations in addition to the thermodynamic nucleation models (Spracklen et al., 2006; Pierce and Adams, 2009; Wang and Penner, 2009; Yu et al., 2010). A recent evaluation, comparing model results to 36 sites around the world, showed that activation-type or kinetic nucleation improves the modeled biases and seasonal cycles (Spracklen et al., 2010).

In this thesis, several steps have been taken to improve the description of new particle formation in the ECHAM5-HAM model. It was shown by Stier et al. (2005) that the model was unable to capture the observed total particle number concentrations,

possibly due to an underestimation of nucleation or emissions, or overestimation of primary emission radii or surface sinks. The original ECHAM5-HAM model included only a parameterization of thermodynamic binary sulfuric acid-water nucleation.

In **Paper I**, activation-type nucleation was introduced to the model concurrent to binary sulfuric acid-water nucleation. The sensitivity of modeled aerosol number concentrations was tested against the activation coefficient, ranging from $2\text{x}10^{-7}$ to $2\text{x}10^{-5}$ s^{-1}. The application of activation-type nucleation was restricted to the boundary layer in **Paper II**. In **Paper III**, also semi-empirical parameterizations of organic nucleation (Paasonen et al., 2010) were implemented in ECHAM5-HAM.

As discussed in Sect. 2.1, a modal aerosol model has difficulties in describing the condensational growth of small particles. Regarding new particle formation, the nucleation mode (particle diameter <10 nm) has to keep track of the nucleated particles (1-2 nm) and follow their growth to the Aitken-mode. To make the task somewhat easier for the model, the nucleation rate can be converted to a formation rate of particles of some larger size, usually 3 nm. Most models using this approach follow the formulation by Kerminen and Kulmala (2002). The growth of the nuclei to 3 nm can be due to sulfuric acid (**Paper I**) or it can contain a contribution from organic vapours (**Papers II and III**). In reality, the growth to 3 nm might take from minutes to hours, but usually the formation rate is applied at the same timestep as nucleation takes place.

Figure 2 shows an example of the simulated development of aerosol number concentrations during May in Hyytiälä, based on simulations with organic nucleation from **Paper III**. The period shows precipitation (white markers at top of figure) on several days. The effect of wet deposition on aerosol concentrations is clearly visible during for example 10–11 May, when the prolonged precipitation cleans the atmosphere from the surface up to 7.5 km altitude. The binary sulfuric acid-water nucleation produces particles mainly between 7 and 10 km altitude, but for example during 2 May, the binary nucleation rates were high even at 5 km altitude. During 2–4 May, the particles nucleated in the free troposphere can be seen to descend into the boundary layer. Boundary layer nucleation is effective throughout the boundary layer, and high concentrations can be seen even up to 2.5 km altitude. When the boundary layer is contracting towards the night-time, a fraction of the nucleated particles is left in the diluting residual layer. During the last half of the month, the particles originating from the boundary layer are clearly separated from the particles nucleated higher up in the atmosphere.

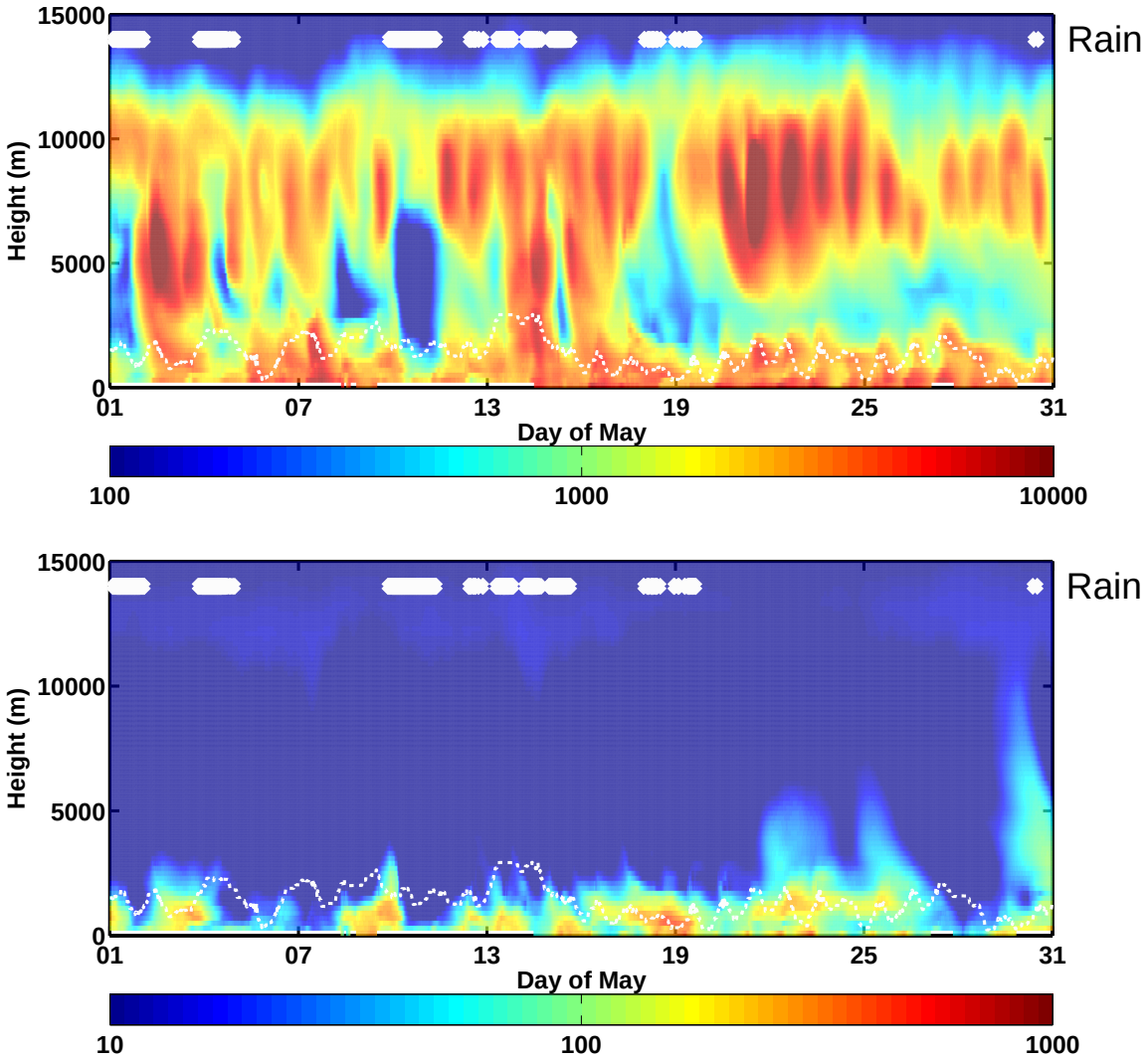

Figure 2: Simulated total aerosol number concentration (cm^{-3}, upper panel) and CCN(0.2%) concentration (cm^{-3}, lower panel) during May in Hyytiälä. Precipitation exceeding a threshold of 0.1 mm/h is indicated with white markers in the upper part of the plot. The dashed line shows the boundary layer height as diagnosed from the model. The simulated concentrations are evaluated in **Paper III**.

Although the application of boundary layer nucleation mechanisms is a clear improvement for modelled number concentrations (Spracklen et al., 2010), current generations of global models are not able to simulate all of the observed features of aerosol number concentrations. In addition to computational issues, such as grid size and description of aerosol size distribution, there are several poorly known source and sink processes.

4 Secondary organic aerosols

Carbonaceous aerosols are generally divided into black carbon and organic carbon. Black carbon (BC), as the name suggests, refers to the light-absorbing part of soot (Bond et al., 1998). In organic carbon (OC), the carbon is bonded to other elements. In practice, atmospheric black carbon aerosols always contain also organic carbon. The OC/BC mass ratio can reach 1.0 in urban background air, or even 0.3–0.4 close to vehicle combustion sources, but OC dominates outside the direct influence of combustion sources (Pio et al., 2011).

Organic aerosol (OA) refers to the particulate organic carbon and the associated elements. Organic aerosol makes a significant, but highly uncertain fraction of the atmospheric fine aerosol mass: even 90% in tropical forests (Andreae and Crutzen, 1997; Talbot et al., 1988; Roberts et al., 2001), and 20-50% in the continental mid-latitudes (Saxena et al., 1996; Putaud et al., 2004). Unlike primary aerosols such as mineral dust and sea salt, a large fraction of OA is formed by gas-to-particle conversion (Kanakidou et al., 2005). Gas-phase volatile organic compounds (VOCs) undergo oxidation by reactions with OH, O_3 and NO_3, eventually forming compounds with lower volatilities. Although there has been a tradition of dividing OA into non-volatile primary organic aerosol (POA) and secondary organic aerosol (SOA) formed via gas-to-particle conversion from low- and semi-volatile compounds, recent studies have shown that the POA emissions are actually very much semi-volatile (Robinson et al., 2007).

The uncertainties in OA budget stem both from emissions and the formation process of OA (Hallquist et al., 2009). Estimates of the global OA source are poorly constrained, ranging from 140 to 910 Tg(C)/yr (Goldstein and Galbally, 2007). Satellite observations have been used to cap the continental OA source to 150 Tg(C)/yr with 80% uncertainty (Heald et al., 2010), while aerosol mass spectrometer observations together with a chemical transport model indicate a continental SOA source between 50 and 380

Tg(SOA)/yr (Spracklen et al., 2011). The anthropogenic contribution to the OA from fossil fuels and biofuels is likely to be small, with sources of 9.1 Tg(OA)/yr and 3.2 Tg(OA)/yr, respectively (Bond et al., 2004). The most important direct anthropogenic OA source is increased biomass burning, which constitutes 34.6 Tg(OA)/yr (Dentener et al., 2006).

Although the sources of VOCs can be attributed to either natural or anthropogenic sources, similar source apportionment of the formed SOA is complicated by the ability of anthropogenic emissions, e.g. NO_x, to influence the SOA formation capability of natural precursors (Hoyle et al., 2011). The anthropogenically modified SOA source could be even 100 Tg(SOA)/yr, of which only 10% can be attributed directly to anthropogenic fossil fuel sources (Spracklen et al., 2011). Including an additional anthropogenically modified SOA source improves model bias near source regions (Heald et al., 2011).

4.1 Biogenic VOC sources

The biosphere provides a source for several biogenic VOCs (BVOCs), including isoprene, monoterpene and sesquiterpene. It has been hypothesised that BVOC emissions could be part of a signalling system between plants ("Talking Trees Hypothesis", Rhoades, 1983): plants affected by stress (from e.g. attack by herbivores) could release BVOCs to warn neighbouring plants (Campos et al., 2008). Plant BVOC emissions can be related to attraction of pollinators or seed dispensers (Dudareva et al., 2006), decreasing competition by inhibiting seeding by other plants (Romagni et al., 2000). The biosphere might have rather direct benefits from the emitted BVOCs: for example, a large part of sesquiterpenes emitted in Amazonian forest is ozonolysed in the canopy, hence reducing the potential plant damage caused by ozone (Jardine et al., 2011).

The emission rates of BVOCs are largely determined by temperature and light conditions (Wiedinmyer et al., 2004). Monoterpene emissions have two sources in the leaf-level: light- and temperature-regulated emission from plant chloroplasts, and temperature-dependent emission from storage (Wiedinmyer et al., 2004). Sesquiterpene emissions correlate with temperature (Jardine et al., 2011).

The estimates of even forest-scale emissions of BVOCs are complicated by the variability in the emitting capabilities of individual plant species. Whether a tree emits isoprene or not can depend from small genetic differences (Wiedinmyer et al., 2004).

However, BVOC emissions can be significantly increased by plant stress, even if BVOC emissions would otherwise be low (Niinemets, 2010).

The global emissions of isoprene and monoterpene range from 412 to 601 Tg(C)/yr and from 30 to 128 Tg(C)/yr, respectively (e.g. Carslaw et al., 2010), however, the SOA production from monoterpenes can be substantially higher than from isoprene (Tsigaridis and Kanakidou, 2007; Hoyle et al., 2007).

Figure 3 compares the sources of OC used in this thesis: wildfires, anthropogenic emissions (biofuel and fossil fuel) and BVOCs. OC emissions from biofuels, originating from burning and making of charcoal, burning of dung and crop residues, are globally three times larger than emissions from fossil fuels (Dentener et al., 2006). Wildfires make local and intermittent contributions to OC, with highest emissions in the tropics but with hotspots around the world. The global emission of OC from wildfires can be even larger than the anthropogenic and biogenic emissions together. BVOCs create a somewhat more evenly distributed source of OC over continents.

4.2 Effects of SOA on particle size distribution

As shown in Figure 1, many primarily emitted particles are assumed to be rather close to, or already at, the size capable of acting as CCN. For example in the case of wildfires, OC, BC and SO_2 are emitted. The fresh primary particles from wildfires can be modeled as 70 nm in diameter (Stier et al., 2005), and the co-emitted SO_2 can grow these particles after oxidation. Very little or no BVOC is needed to grow the particles to CCN size, although areas of high wildfire emissions often have a strong BVOC emission. Anthropogenic combustion aerosols (e.g. OC in Figure 3, left panel) are smaller in size and their CCN forming capability is more sensitive to the growth from BVOCs.

Nucleated particles have been observed to grow up to diameters of a few tens of nanometers in a few hours. Even if the nucleation rate could be explained by sulfuric acid, it can only cover a fraction of the observed particle growth (Boy et al., 2003, 2005; Fiedler et al., 2005). It has been suggested that the additional growth would be provided by low-volatile organic vapours (Yu, 2011; Riipinen et al., 2011). Increased SOA mass acts as sink for both condensing vapours and small particles, decreasing nucleation rates and possibly the total number concentration. On the other hand, increased

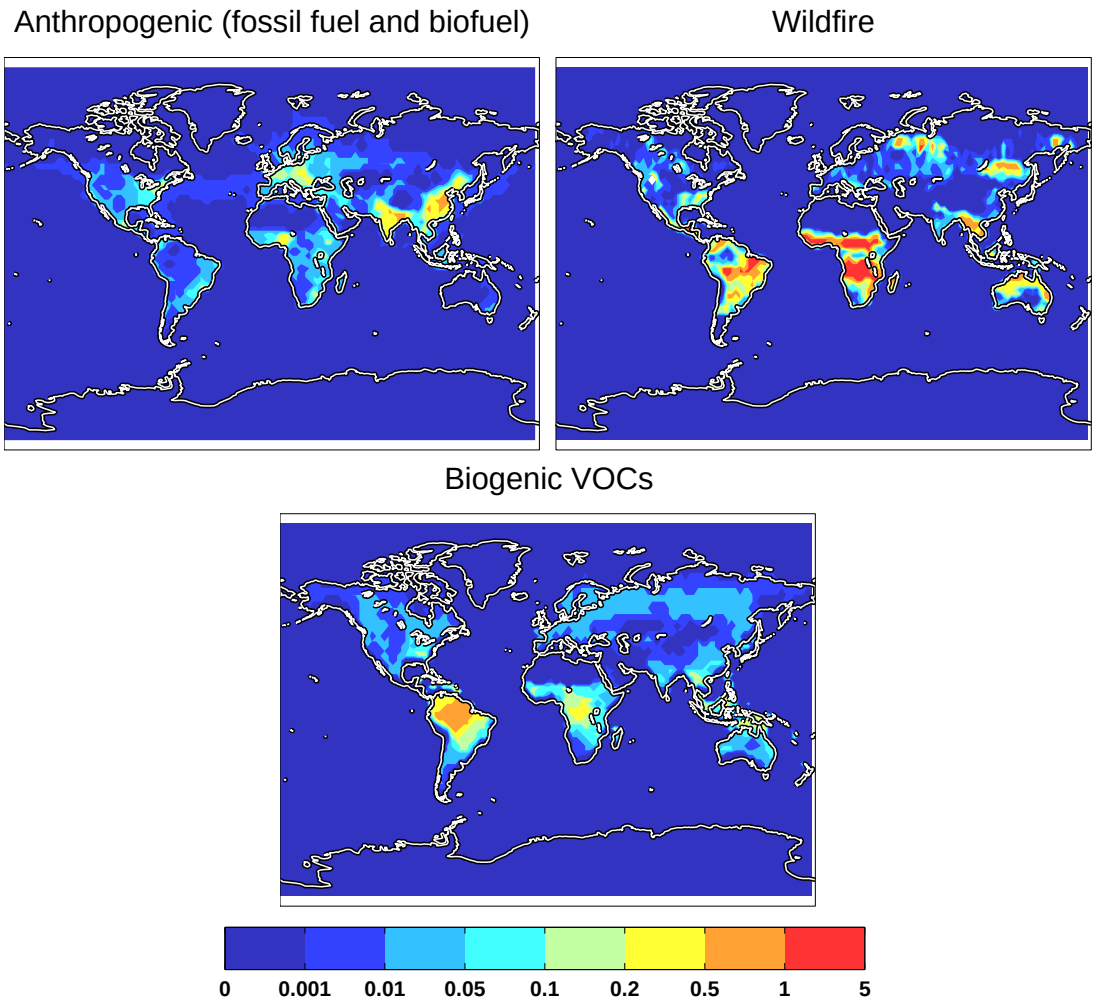

Figure 3: Present-day emissions of OC (kg m^{-2} yr^{-1}) from anthropogenic sources (including fossil fuel and biofuels) (Dentener et al., 2006), wildfires (van der Werf et al., 2004) and biogenic VOCs (Guenther et al. (1995) monoterpene emissions scaled by 0.15).

condensation helps the freshly-formed particles to grow faster, increasing their survival probability. Then again, more particles competing on the condensing vapours slows down the conversion of CN to CCN.

Figure 4 shows the effect of BVOC on CCN concentration, based on simulations in **Paper III**. In Siberia, monoterpene emissions from boreal forest can increase CCN by even 50% or more. The effect of the boreal forest emissions is seen transported over to the Arctic. The long-range effects of BVOCs are also visible in the Pacific outflows from

Asia and South America, and in the mid and high latitudes in the Southern Hemisphere, which are affected by BVOC emissions from South America, Africa and Australia. In terms of absolute CCN concentration, the area most affected by BVOCs is China with high primary aerosol and SO_2 emissions. In the US, the increased condensation sink from BVOCs induces a large decrease on nucleation rates, total particle concentrations, and also on the CCN concentrations.

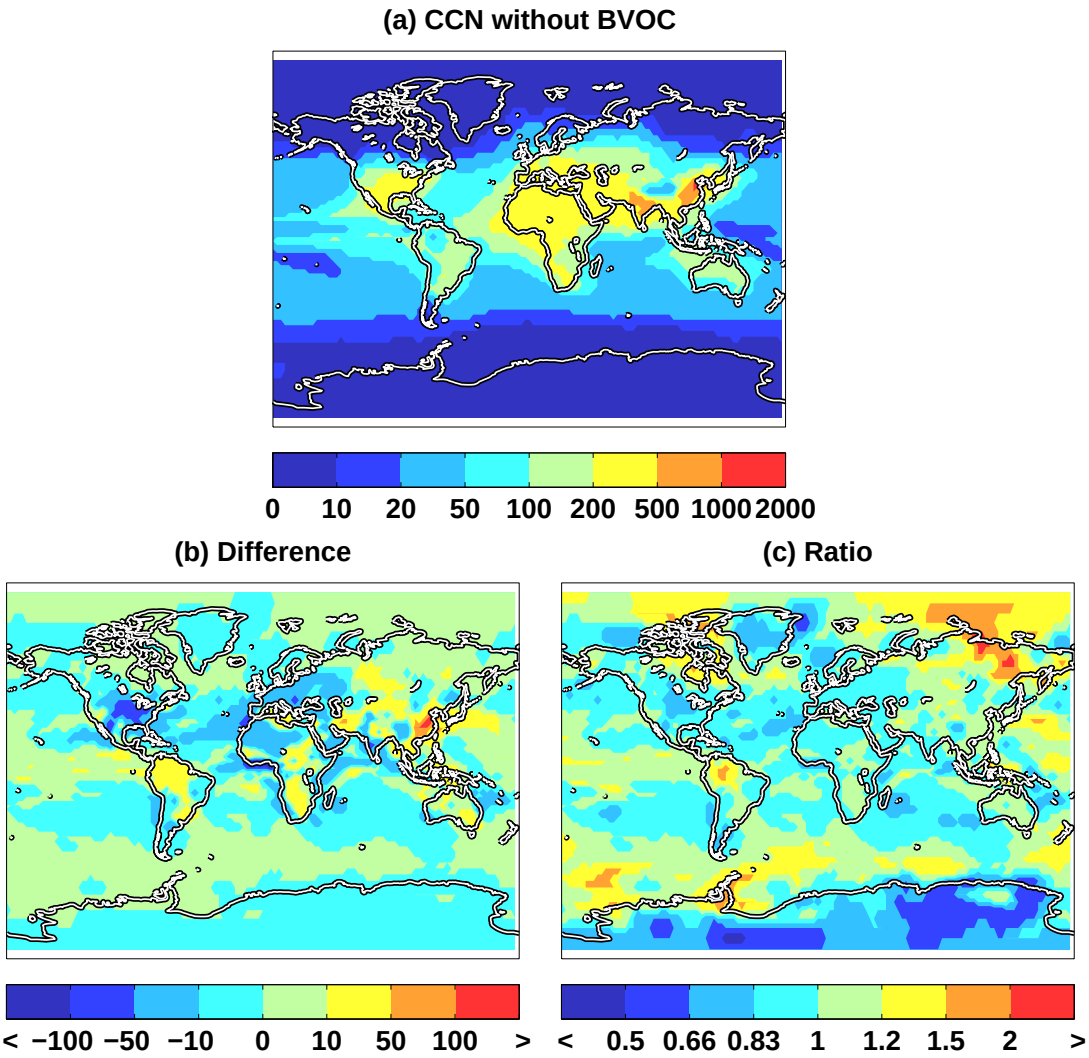

Figure 4: (a) CCN(0.2%) concentration (cm^{-3}) without BVOC, (b) absolute increase in CCN(0.2%) concentration (cm^{-3}) due to BVOCs, and (c) relative increase in CCN(0.2%) concentration due to BVOCs. Results are based on simulations from **Paper III**.

4.3 Modeling SOA formation in global scale

Although organic compouds have been integrated in global aerosol models for over 15 years (Liousse et al., 1996), models still generally underestimate the observed organic aerosol mass (Heald et al., 2010, 2011; Spracklen et al., 2011). However, it could be that the importance of POA is even overestimated, and the OA underestimation would rise from uncertainties in modelling SOA formation (Kanakidou et al., 2005). In some cases, an increase by a factor of 100 in the gas-particle partitioning coefficients might be needed to match the model results to observations (Hodzic et al., 2009; Trivitayanurak et al., 2012).

The vast amount of different organic compounds emitted to the atmosphere possesses a problem for large scale models: it is not sensible to try to include individual compounds in the model, but instead lump different species together based on their properties. A general modeling problem lies in the gas-aerosol partitioning of the organics, since the range in volatilities of atmospheric organics is huge.

Until recently, many global aerosol models either ignored SOA formation, or treated SOA formation as primary OA emission (Textor et al., 2006). A simple way to approach SOA formation is to assume a precursor emission (e.g. monoterpene) and a fixed fraction of how much precursor gas is partitioned irreversibly in the aerosol phase. To save computational costs the partitioning can be done during one timestep, and disregarding the gas-phase organics: this way, no additional tracers are needed for the organics.

A two-component model assumes that the oxidation of a precursor compound produces effectively three end-products: volatile, semi-volatile and non-volatile (Odum et al., 1996). One approach to modeling SOA precursors is the volatility basis set: the organic vapours are lumped into bins according to their volatility (Donahue et al., 2006). The emissions from a single source can contain either a single volatility or a distribution of volatilities. Oxidation moves the compounds to bins of lower volatility. The approach can be extended into two dimensions, by including oxygen content (O:C ratio) in addition to volatility (Donahue et al., 2011, 2012).

There are several levels of details to approach the condensation and partitioning of organic compounds in global models. The simplest approach, used in many earlier global models, is to assume that SOA is formed with a fixed size distribution, and

model SOA basically as POA (e.g. Stier et al., 2005). In a kinetic approach, the organic vapours are assumed non-volatile and distributed to the aerosol phase according to the condensation sink (Spracklen et al., 2010). Thermodynamic partitioning assumes that the organic vapours are in equilibrium with the aerosol phase (O'Donnell et al., 2011). The model can also assume a combination of kinetic and thermodynamic partitioning (Riipinen et al., 2011).

Using the kinetic approach, organic vapours can condense on the newly-formed particles and explain their observed growth (Riipinen et al., 2011). However, the thermodynamic partitioning, usually based on absorbtion of the condensing organics, leads to condensational fluxes mainly on the larger end of the particle size spectrum. This leads to too small growth for small particles, an increase of the condensation sink of the large particles, and a decrease in the nucleation rates (O'Donnell et al., 2011). It could be that a hybrid approach is needed to fully quantify the effect of especially anthropogenic organics (Riipinen et al., 2011).

In this thesis we have improved the description of SOA in the ECHAM5-HAM model. Originally, ECHAM5-HAM first assumed that a fraction of 0.15 of monoterpene emissions formed BSOA. This BSOA mass was then distributed to the aerosol phase with prescribed assumptions of the solubility and size distribution. 65% of the formed BSOA was assumed soluble, and was partitioned 50/50 to the soluble Aitken and accumulation modes. The insoluble BSOA, 35%, was then partitioned to the insoluble Aitken mode. The gas-to-particle conversion was assumed to take place during the timestep of the emission in the lowest model layer.

In **Paper I**, we removed the prescribed assumptions of BSOA solubility and size distribution. We assumed that the low-volatile organic vapours would condense on the particle phase according to the condensation sink, which was calculated separately for each of the seven log-normal modes. The original M7 did not include organic mass tracers in the nucleation mode or the insoluble accumulation and coarse modes, and these three additional tracers needed to be included. **Paper I** assumed that the formation of SOA took place in the lowest model level, i.e. near ground surface, while **Papers II and III** first distributed the SOA precursor to the boundary layer. Due to low temperatures, a significant fraction of SOA formation might actually occur in the free troposphere (Tsigaridis and Kanakidou, 2003). Assuming SOA formation only in the boundary layer might lead to underestimating the lifetime of SOA.

It is natural that the original assumptions in ECHAM5-HAM BSOA formation might perform adequately in environments with similar sinks of Aitken and accumulation modes, but the prescribed size distribution could not take aerosol dynamics into account. It was shown in **Paper I** (Figure 5) that in the tropics and parts of Asia, the flux of organics to accumulation mode is more than three times greater than the flux to Aitken mode. In pristine environments, especially in high latitudes, the organics were mainly condensing in the dominating Aitken mode. By allowing the organics to condense with even likelyhood to soluble and insoluble modes, the organic flux to soluble modes was on average higher than the original assumption of 65%. The insoluble modes made a significant condensation sink only in areas of high emissions of BC and dust.

The sensitivity of aerosol and cloud droplet number concentrations was tested against the amount of formed BSOA. With boundary layer nucleation included, the increase of BSOA yield from 7% to 15% lead to a change in CN concentrations ranging from -5% to +15% (**Paper I**, Table 2). Except in the marine locations of ACE-1 and ACE-2 campaings, the increased BSOA formation lead to on average 12% more CCN (particle diameter d_p >100nm). However, the effect of BSOA of CCN can be even reversed if boundary layer nucleation is not implemented, as seen in Table 2 of **Paper I**. This occurs because BSOA acts to increase the condensation sink instead of providing particle growth.

Spatial and temporal differences in BVOC emissions can be important for aerosol concentrations. The diversity in the applied BVOC emission datasets arises from the emission algorithm, vegetation description and its spatial distribution, and the climate used with the emission model. Most global aerosol models use emission datasets based on Guenther et al. (1995). Very few studies have addressed the sensitivity of aerosol number concentrations to the underlying BVOC emission. Spracklen et al. (2008) showed that a factor of 10 was needed for the GEIA BVOC emission inventory (based on Guenther et al., 1995) to explain the observed monoterpene concentration in Hyytiälä in March. The increase in CN concentration due to the 10x organics was about 30% in Hyytiälä. In **Paper III**, BVOC emission datasets from two mechanistically different BVOC models were applied in ECHAM5.5-HAM2, showing large variability in CN and CCN concentrations due to the selection of BVOC emission model.

Figure 5 shows the ratio of particle organic mass versus sulfate mass in the nucleation mode from the lowest model level of ECHAM5.5-HAM2. Sulfate mass is dominant in

areas with significant anthropogenic emissions, whereas in the tropical South America, nucleation mode particles contain 10 times more organics than sulfate. In addition to tropics, organics make a major contribution to nuclei growth in the continental Northern Hemisphere, around 50°-80°. This indicates that globally, organics can be a major contributor to the growth of freshly-nucleated particles.

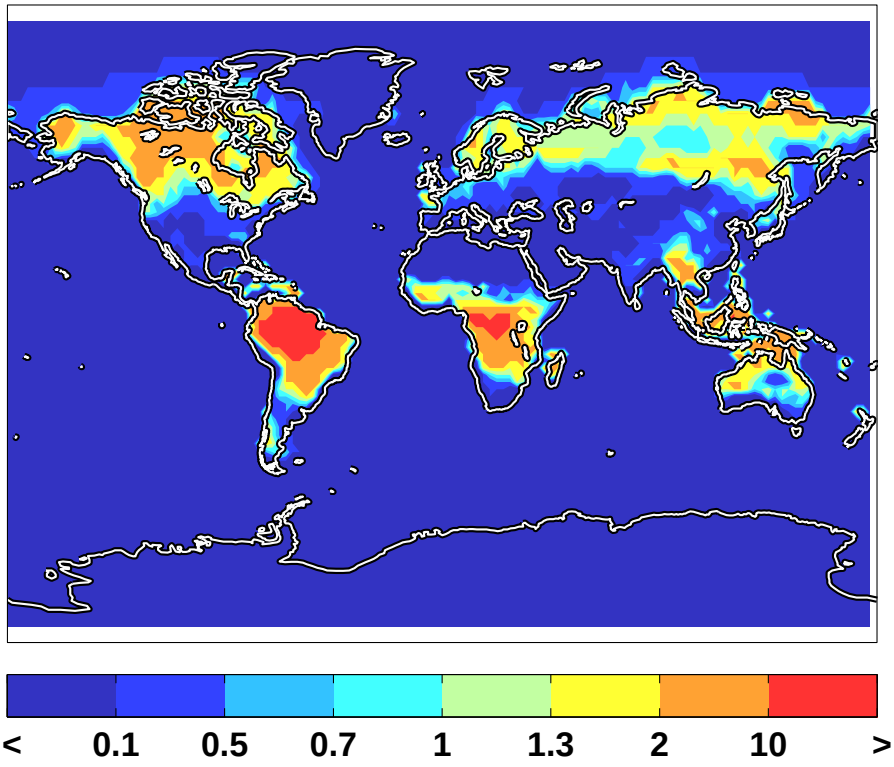

Figure 5: Annual average ratio of organic versus sulfate mass in the nucleation mode, based on simulations in **Paper III**.

5 Aerosol-cloud interactions

5.1 Cloud types

Clouds cover 55–60% of the Earth's surface on an annual average (Cotton and Anthes, 1989). The bright white color creates a strong contrast above dark surfaces, such as oceans and boreal forests. Indeed, while the albedo of coniferous forest can be as low

as 0.083 (Betts and Ball, 1997), the cloud albedo ranges on average between 0.4 and 0.5 (Han et al., 1998). In locations with a high surface albedo, such as the Antarctic, the albedo-increasing effect of clouds is small.

Clouds form when water vapour in supersaturated state condenses to liquid droplets. The supersaturation can be achieved in several ways, usually by lifting warm air upwards by convective updrafts or by collision of air masses of different densities. Orographic clouds form when a moist air mass is forced to move upwards against a slope. Also, horizontally moving air masses converging near surface lead to upward motion.

Clouds are found throughout the troposphere and even in the stratosphere. The radiative effects of a certain cloud depend on the cloud top height and cloud optical thickness. Clouds with base at low altitudes can extend over vast areas of marine boundary layer (marine stratocumuli) or extend several kilometers in the vertical (cumulonimbus). Low-level clouds are responsible for half of the cloud radiative effect (Chen et al., 2000). High-level clouds, such as cirrus, are composed of ice crystals, and are generally too thin to affect solar radiation budget. However, high-level clouds absorb and reflect longwave radiation back towards the surface.

Although the spatial extent and radiative effect of orographic clouds is not as significant as some other clouds types, they are extremely important in controlling the spatial distribution of precipitation around hills and mountains (Smith, 1979).

5.2 Relations between clouds and aerosols

It is interesting to think what would happen to clouds if the Earth's atmosphere was free from aerosol particles: supersaturated water would not have a surface to condense to, and cloud droplets would need to nucleate homogeneously. In practice this would take too much energy and no clouds would form. In present-day atmosphere, cloud droplets always form on an existing aerosol particle of either natural or anthropogenic origin. Although human activitites have increased the number of available CCN, there has undoubtedly been enough natural CCN for cloud formation in the past (Andreae and Rosenfeld, 2008).

Aerosols have also non-microphysical effects on clouds: aerosols absorbing short-wave radiation cause warming of atmosphere and reduction of relative humidity. The so-called semi-direct effect was originally introduced as a cloud-cover reducing effect

(Hansen et al., 1997), but actually the effect depends on the cloud type and the altitudes of the cloud and the absorbing aerosol (Koch and Del Genio, 2010). The semi-direct effect can play an important role for example over northern Indian Ocean, which receives high concentrations of black carbon from southern Asia (Ackerman et al., 2000). This polluted air mass can reduce the relative humidity and lead to a 5-10% decrease in cumulus cloud cover (Ackerman et al., 2000).

While aerosols affect cloud properties, clouds influence both aerosol processing and their transport. In-cloud oxidation could make 90% of the chemical sink of SO_2 (Pham et al., 1995). Convective systems play a crucial role in the transport of aerosols to higher altitudes (Cui and Carslaw, 2006).

5.3 Cloud droplet activation

Cooling of an air parcel leads to increasing saturation ratio of water vapour which starts to condense on available surfaces. The surface, for example a hygroscopic salt particle, stays in equilibrium with the surrounding air. At first, the water could be condensing on a rather small fraction of the particle surface area, gradually covering the whole particle. Should the supersaturation continue to increase, the droplet size might exceed the activation radius: after this point, water continues to spontaneously condense on the droplet. The condensation of water is thereafter limited by depletion of water from the gas phase.

The above description of cloud droplet activation according to the Köhler theory is in the atmosphere complicated by (partly) insoluble cores, co-condensation of other vapours than water, and formation of films on the surface of the aqueous phase (McFiggans et al., 2006).

5.4 Aerosol indirect effects

Aerosol indirect effect refers to a change in cloud properties due to a perturbation in aerosol number concentration, and it is traditionally divided into two parts. The first indirect effect, also known as Twomey effect, describes the decrease in cloud droplet size due to increased cloud droplet number concentration (CDNC), leading to increased cloud albedo (Twomey, 1974). The second indirect effect contains several mechanisms

beyond the Twomey effect. According to the Albrecht effect, increase in cloud droplet number can lead to increased liquid water path (LWP) and albedo via reduced collision-coalescence and diminished precipitation (Albrecht, 1989). Both Twomey and Albrecht effect indicate an increase in cloud albedo from increased aerosol number. There are also several mechanisms that could work in the opposite direction: increase in CDNC could lead to stronger entrainment, a decrease in LWP and lower albedo (Chen et al., 2011). Wood (2007) suggested that reduced precipitation in drizzling clouds would also act to increase turbulent kinetic energy (TKE) via reduction in below-cloud evaporative cooling and in-cloud release of latent heat. In non-drizzling clouds the increased CDNC would make evaporation more efficient, which would also tend to increase TKE (Wang et al., 2003; Xue and Feingold, 2006; Hill et al., 2008). The increase in TKE would then act to amplify entrainment, lowering the albedo. Without drizzle, increase in cloud water and evaporation in entrainment regions would also increase entrainment (Ackerman et al., 2004; Bretherton et al., 2007; Hill et al., 2009).

5.5 Modeling aerosol-cloud interactions in global scale

As the horizontal resolution in global climate models ranges from tens to hundreds of kilometers, it is clear that the models can not fully resolve cloud properties. Parameterizations are needed to address the subgrid-scale properties, such as spatial variations of relative humidity, updraft velocities and cloud cover.

Before the early 2000s, global models relied on empirically-derived relations between aerosol mass and CDNC (Boucher and Lohman, 1995; Jones et al., 1994). Due to the complexity of the aerosol-cloud coupling, aerosol mass is not a good proxy for CCN. To date, a handful of parameterizations exist for the relation between aerosol and cloud droplet number concentrations.

One of the earliest parameterizations is described in Lin and Leaitch (1997). The parameterization is based on aircraft measurements of number concentrations in North America. The number concentration of particles with wet radius larger than 35 nm is given to the parameterization, which is then used to calculate the number of activated particles. The limited number of measurements and the lack of information on composition raises some doubt to apply the parameterization for all cloud types and conditions in the global scale, however, the benefits over a mass-based CDNC relation

are indisputable. The Lin and Leaitch (1997) parameterization was used in **Papers I and II**.

Based on earlier work by Twomey (1959) and Ghan et al. (1993), Abdul-Razzak et al. (1998) provided a cloud droplet activation parameterization for a single lognormal aerosol mode. The parameterization is based on Köhler theory to calculate the number of activated particles from the aerosol size distribution and maximum supersaturation reached. Unlike in Lin and Leaitch (1997), the aerosol composition is accounted for in Abdul-Razzak et al. (1998). The multimodal version of the parameterization (Abdul-Razzak and Ghan, 2000) and the sectional version (Abdul-Razzak and Ghan, 2002) have become widely used in global models, partly due to their simplicity. The parameterization was used in **Papers III and IV**.

The formulations of Nenes and Seinfeld (2003) added some complexity in the aerosol mixing state and chemical composition. Later, the modifications by Fountoukis and Nenes (2005) eased the applicability of these parameterizations to global models.

The above parameterizations for the cloud droplet activation do not take into account the possible effects of soluble trace gases, such as HCl or HNO_3. These gases can condense to the aqueous phase of the particle together with water, increasing the amount of soluble material in the droplet (Kulmala et al., 1993). The increased hygroscopic mass can activate particles at lower RH and increase the fraction of activated particles. The effect of soluble trace gases can be integrated to the one of the above cloud activation parameterizations (Romakkaniemi et al., 2005). **Paper IV** studied the effect of nitric acid on cloud activation.

Different parameterizations for cloud droplet activation lead to variable results in terms of modeled CDNC and its spatial distribution. Until today, a thorough comparison of the performance of the different schemes in climate models is still missing, and none of the schemes can be claimed to be superior (Ghan et al., 2011). However, the cloud droplet activation is a critical step towards quantifying the aerosol indirect effects.

6 Present-day and future aerosol climate forcing

6.1 Quantifying aerosol-climate interactions

Aerosols affect Earth's energy balance directly by scattering and absorbing radiation, and indirectly by changing cloud properties. These perturbations affect both atmospheric temperatures (e.g. absorption of solar radiation by aloft black carbon) and surface temperatures (less solar radiation reaching the surface).

To estimate the actual response of atmospheric temperatures to aerosol effects requires an atmospheric model coupled to an ocean model, and tens of years of simulation to reach equilibrium with new aerosol conditions (e.g. Kloster et al., 2010). To evaluate aerosol effects more efficiently, intermediate variables can be extracted from even short simulations. For the aerosol direct effect, typical such variable is the aerosol optical depth (AOD), which is a measure of the extinction of radiation due to scattering and absorption.

The indirect aerosol effect, being more complex in nature, is difficult to be summarized with a single variable. The quantification of aerosol indirect effect requires information of both 3-D cloud cover, effective cloud droplet radii and LWP. If the cloud water and cloud heights can be assumed constant, then the changes in the cloud albedo (1st indirect effect) can be accessed via changes in cloud droplet number concentrations (Twomey, 1991)

$$\Delta Rc = Rc(1 - Rc)/3ln((CDNC_2/CDNC_1)) \tag{2}$$

where $CDNC_1$ and $CDNC_2$ are from the simulations to be compared, and Rc is the cloud albedo.

The concept of radiative forcing (RF) is developed to help the quantification of climate effects without the need for full climate simulations. The Intergovernmental Panel on Climate Change (IPCC) defines the radiative forcing as 'the change in net (down minus up) irradiance (solar plus longwave; in W m^{-2}) at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values' (Ramaswamy et al., 2001; Forster et al., 2007). The RF has been successfully applied with

long-lived greenhouse gases and solar insolation. However, there are limitations in the relationship between an RF and the related climate response, especially with aerosol perturbations (Forster et al., 2007). The traditional RF applies only for instantaneous radiative perturbations when, for example, increased reflectance from increased amount of aerosols or cloud droplets modifies the radiative fluxes. The RF does not include, by definition, fast feedbacks arising from indirect effects beyond the cloud albedo effect (changes in precipitation, cloud cover) (Lohmann et al., 2010).

When quantifying the aerosol effects, calculation of RF would require fixing of the model meteorology at the unperturbed state, while allowing the stratosphere to adjust to the perturbation. This can be rather closely achieved by nudging techniques, which push the model temperature, surface pressure, vorticity and divergence towards a prescribed state, usually towards reanalyzed meteorological data (e.g. ERA40, INTERIM). Of the indirect aerosol effects, only the cloud albedo effect can be considered as an RF, which means that the cloud droplet number concentration has to be prescribed in the calculation of the precipitation formation.

To include indirect aerosol effects beyond the cloud albedo effect, one has to go beyond the traditional RF. Concepts of "fixed sea surface temperature (SST) forcing" (Hansen et al., 2002) and "quasi forcing" (Rotstayn and Penner, 2001) were introduced to allow for changes in tropospheric temperatures and fast feedbacks. After fixing the surface temperatures (either sea, or sea and land) to prescribed values, the aerosol effects can be calculated as radiative flux perturbations (RFPs) (Lohmann et al., 2010). The concept of fixed-SST RFP was used in **Papers II, III and IV**.

In the case of IPCC definition, the anthropogenic forcing is calculated as a change in radiative flux relative to the year 1750. For many compounds, there is still somewhat reliable information on the emissions in the year 1850, and the emission datasets for the year 1750 are barely scaled by e.g. population density. Hence, many studies use the year 1850 as the reference year (e.g. Merikanto et al., 2009). Forcing often refers to the (anthropogenic) perturbation since the reference year, but for example cloud forcing refers to a measure of the instantaneous radiative effect of clouds. Table 1 lists some terms used for aerosol climate effects.

Table 1: Terms in literature related to aerosol effects and forcings.

CRE, CRF, (SW)CF	(Short-wave) Cloud (Radiative) Effect/Forcing
SWARF	Short-wave aerosol radiative forcing
DRE,DRF	Direct Radiative Effect/Forcing
AIE,IAE,AIF,IAF	Aerosol Indirect Effect/Forcing

6.2 Changes in aerosol and precursor emissions

Before the beginning of industrialization, anthropogenic particle emissions originated from wood and coal burning, both used in heat generation and cooking. While coal combustion has remained as an important emission source, the consumption of petroleum products has gained a substantial contribution of the total particle emissions. The currently increasing use in biofuels, although beneficial with respect to CO_2 emissions, might have adverse effects from increased aerosol and precursor emissions (Tiwary and Colls, 2010). Although human activities have most probably increased the amount of wildfires globally, anthropogenic suppression of forest fires might have led to a decrease in forest fires in certain regions, compared to pre-industrial (Brenkert et al., 1997; Dentener et al., 2006).

The developments in fuel refining together with burning and filtering technologies have induced changes in the emission factors of particulate matter (g(PM)/kg(fuel)). The potential effects on the emitted primary particle size distribution are generally overlooked.

Many natural aerosol sources will respond to the changing climate, e.g. changes of temperature or precipitation (Carslaw et al., 2010). These aerosol feedbacks are said to be positive (negative) if they act to increase (decrease) the signal they respond to.

6.2.1 Sulfur dioxide

Large quantities of sulfur is naturally emitted from volcanoes (7.5–13 $Tg(SO_2)$/yr (Andres and Kasgnoc, 1998; Halmer et al., 2002)), wildfires, and as DMS from the oceans (16–54 Tg(S)/yr (Kettle and Andreae, 2000)). The anthropogenic versus natural contribution on wildfires is difficult to quantify, but the SO_2 emissions from wildfires have increased from 1.46 $Tg(SO_2)$/yr in the year 1750 to 4.1 $Tg(SO_2)$/yr in the year 2000 (Dentener et al., 2006).

The anthropogenic SO_2 emissions have increased from 2 to 131 $Tg(SO_2)/yr$ between years 1850 and 1980 (Smith et al., 2011). Throughout this time period, the main source for SO_2 has been the combustion of coal, while emissions from petroleum combustion have increased mainly after the 1940's (Smith et al., 2011).

Sulfur emissions have direct environmental effects. Acid rain troubled Europe in the 1970's, and deposition of sulfur has caused damage to forests and soils (Nellemann and Thomsen, 2001). With imposed regulations, SO_2 emissions started declining in North America and Europe already in the 1970's, while emissions in for example China and India have continued to increase until 2005 (Smith et al., 2011). However, there are indications that SO_2 emissions in China might already have decreased in the recent years (Lu et al., 2010). Globally, SO_2 emissions might have decreased to 107 $Tg(SO_2)/yr$ in the year 2000.

The A2 scenario in the IPCC SRES (Nakicenovic and Grübler, 2000) predicted that the SO_2 emissions will increase for a few decades, and then decrease close to present-day values. The near-future increase was seen also in other scenarios (A1B, A1FI and B1), but the decrease until the end of the 21st century is more clear in these scenarios. The emission pathways developed for the next IPCC report, "Representative Concentration Pathways" (RCPs), are unanimous in predicting a strong decline in the SO_2 emissions by the year 2100 (Lamarque et al., 2011). In one scenario the decline is more steady and most of the decrease occurs in the first half of the century (van Vuuren et al., 2007), while one shows a fast decline after 2060 (Fujino et al., 2006).

6.2.1.1 DMS feedback

Perhaps the most intensively studied aerosol feedback is the CLAW hypothesis (Charlson et al., 1987), which links increasing temperatures to enhanced phytoplankton growth and increased DMS emissions, which could provide more CCN and hence a cooling effect. However, recent findings indicate that the CCN concentration is not very sensitive to changes in DMS emission (Woodhouse et al., 2010), and that the marine CCN production is far more complex than suggested in the CLAW hypothesis (Quinn and Bates, 2011).

The projected changes in DMS emission until the year 2100 vary greatly. Based on an increase of 1.76 K in surface temperature, Ramaswamy et al. (2001) estimated

an increase of 6.5% in global DMS emission. Using a coupled atmosphere-ocean-biogeochemistry model, Stier et al. (2006) found that the increased ocean mixed-layer depth actually leads to a decrease of 8% by the year 2100.

In **Paper II**, the effect of a future increase in DMS emission was studied. A rather high DMS emission increase of 10% was used. The increased DMS led to increased particle nucleation and growth, and eventually to a 2% increase in the cloud droplet number concentration. Although the introduced negative forcing of -0.12 W m^{-2} is small compared to the change in the anthropogenic forcing by the year 2100, the results support a negative DMS feedback.

6.2.2 Black carbon

Black carbon or soot is linked to both adverse health effects and climate warming. It has been hypothesized that soot from fossil fuel and biofuel combustion could be the second-most important climate warming contributor, and that elimination of soot from these sources might reduce global surface temperatures by 0.4–0.7 K (Jacobson, 2010). When reducing BC and OC emissions simultaneously by 50% from fossil fuels, biofuels and biomass burning, the gained negative forcing of -0.12 W m^{-2} (from reduced BC absorptive heating) could be offset by a reduction in the aerosol indirect effect, leading to a net forcing of +0.19 W m^{-2} (Chen et al., 2010). Although mitigation of BC is a promising way for reducing climate warming in a short timescale, the aerosol-cloud coupling complicates the resulting climate benefits.

6.2.3 Organic carbon

OC emissions from wildfires and biofuels have increased since 1750 by 170% and 480%, respectively. Currently, fossil fuels make only about 5% of the global OC emissions (Dentener et al., 2006). The OC emissions reductions in the RCP pathways range from 10% to 46% (Lamarque et al., 2011), the difference coming mainly from uncertainties in deforestation and savannah burning.

6.2.3.1 BVOC feedback

As discussed in Sect. 4.1, the biosphere is a significant source of BVOCs. The biosphere can react to climate change in a multitude of ways: movements of vegetation types, changes in productivity, increased emissions due to stress. The potentially increasing BVOC emission could lead to increased particle growth, more numerous CCN, and eventually to brighter clouds and cooling (Kulmala et al., 2004a). The BVOC-aerosol-climate feedback is further complicated by the gas-aerosol partitioning as discussed in Sect. 4.2.

The warming climate could increase isoprene emissions by 22–55% and monoterpene emissions by 19–58% by year 2100 (Carslaw et al., 2010). There is indication that some BVOC emissions could be inhibited by the increasing CO_2 concentrations (Arneth et al., 2007). If the proposed CO_2 inhibition mechanism is taken into account, isoprene and monoterpene emissions could actually decrease until year 2100 by 8% and 7%, respectively (Carslaw et al., 2010). In **Papers II and III** the feedback was concluded plausible, although subject to several uncertainties.

6.2.4 Nitrogen oxides

Nitrogen oxides (NO_x = NO + NO_2) are produced naturally by lightnings and in soils. The lightning emissions have been extremely uncertain in the past decades, ranging from 1.2 Tg(N)/yr (Borucki and Chameides, 1984) to 200 Tg(N)/yr (Franzblau and Popp, 1989), due to uncertainties in emitted molecules per one flash (Biazar and McNider, 1995). The current estimates ranging from 1 to 4 Tg(N)/yr are comparable to the natural biogenic soil emissions (Delmas et al., 1997).

Globally, 83% of the NO_x emissions are anthropogenic (Delmas et al., 1997). Production of NO_x favors high temperatures, and the combustion of fossil fuels in transportation, heating and power generation makes the major part of the anthropogenic emission of 15–29 Tg(N)/yr (Delmas et al., 1997).

Kulmala et al. (1995) discussed the relative roles of SO_2 and NO_x emissions, showing that the ratio of NO_x to SO_2 emission has been increasing throughout the 20th century. Figure 6 shows the emission ratio of NO_x to SO_2 based on the four RCP scenarios (van Vuuren et al., 2011). All future pathways indicate a increase from the present-day ratio

of 0.7 to 0.8–1.1 until the year 2030. By the end of the century, the NO_x emissions will be already 1.5-2.5 times the SO_2 emissions.

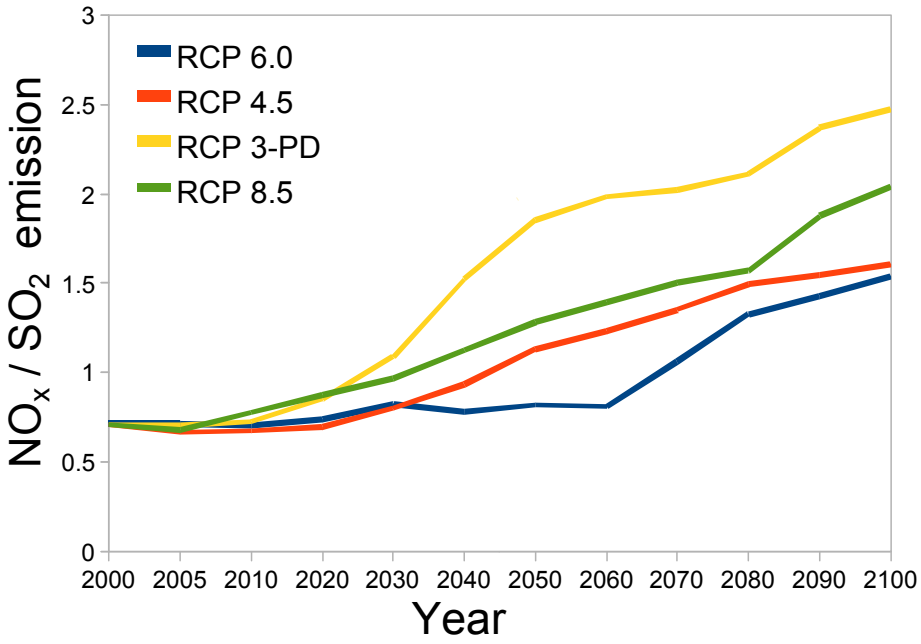

Figure 6: The ratio of emissions of NO_x (Tg(N)/yr) and SO_2 (Tg(S)/yr) from the year 2000 to year 2100. Four future emission pathways are shown (Lamarque et al., 2011).

The relative importance of NO_x could outplay the role of SO_2 in the future. Adams et al. (2001) showed that the anthropogenic direct forcing of nitrate (sulfate) aerosols could increase (decrease) from -0.19 W m^{-2} (-0.95 W m^{-2}) in the present-day to -1.28 W m^{-2} (-0.85 W m^{-2}) in the year 2100. However, this work was based on the SRES A2 scenario with only a slight decrease in SO_2 emission and with even tripled NO_x emissions. Even with a decreasing NO_x emissions in the newer emission pathways, increases in future ammonia concentrations could increase the direct radiative forcing due to ammonium nitrate aerosols (Lamarque et al., 2011).

The potential indirect effect of soluble trace gases was proposed already 20 years ago (Kulmala et al., 1993), but no estimates of the climate implications have been quantified. NO_x is a precursor of nitric acid. It is shown in **Paper IV** that the present-day cloud albedo effect of NO_x via the effect of HNO_3 on cloud activation could be -0.32 W m^{-2}. Due to the decreasing aerosol concentrations, the future cloud albedo effect could strengthen to -0.37 W m^{-2}, when assuming present-day HNO_3 concentrations.

Despite the current generally decreasing trend of both global SO_2 and NO_x emissions,

the relative roles of the two compounds on radiative forcing might certainly change during the 21st century.

6.3 Evolution of particle number concentrations

The aerosol number concentrations respond to changes in concentrations of anthropogenic and biogenic precursors. In addition to modifications in emissions, climate change can influence the number concentrations more directly. As thermodynamic models of nucleation show that increasing air temperatures would act to slow down nucleation rates, Yu et al. (2012a) suggested that climate warming would lead to a decrease in aerosol number concentration. Changes in atmospheric temperatures can also modify the partitioning coefficients of organics, with warmer climate resulting in relatively more organics residing in the gas-phase (Tsigaridis and Kanakidou, 2007; Heald et al., 2008).

It is shown in **Papers II and III** that the global CCN concentration is sensitive to the anthropogenic emissions of SO_2, BC and OC. If we think that the anthropogenic SO_2 emission is a proxy for the anthropogenic perturbation on CCN, and that the biogenic VOC emissions make a linear contribution, we can plot the evolution of the CCN based on historical and projected global SO_2 emissions (Figure 7). It should be kept in mind that the SOA formation model used in this thesis can not take into account all interactions between anthropogenic emissions and biogenic precursors (Spracklen et al., 2011; Hoyle et al., 2011), which would imply a cross-term between the BVOC and SO_2 emissions.

6.4 Aerosol forcing

Information on the present-day aerosol forcing is crucial when determining the future direction of climate. A weak aerosol forcing implies that the climate is not very sensitive to the added GHGs, while a strong aerosol forcing a large climate sensitivity (Andreae et al., 2005). The combination of a strong present-day forcing, high climate sensitivity and a reduction in future aerosol forcing would increase the probability of a significant climate warming.

Significant amount of work has been done to estimate the present-day aerosol forcing.

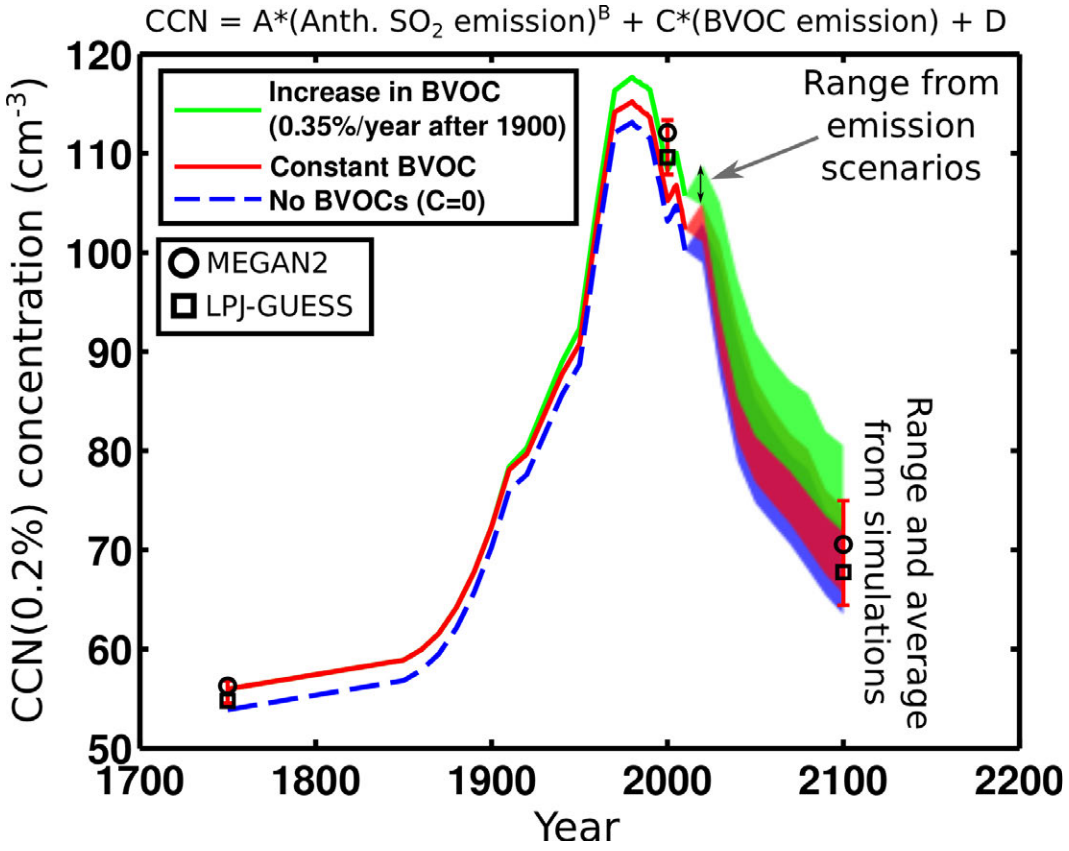

Figure 7: Global average CCN(0.2%) concentration from the year 1750 to 2100, parameterized by anthropogenic SO_2 emission, a linear contribution from BVOC emission, and a background concentration. The parameterization is based on simulations in **Paper III**, and simulation results are shown for years 1750, 2000 and 2100. The SO_2 emissions are from Dentener et al. (2006) (year 1750), Lamarque et al. (2010) (years 1850–1970), AeroCOM-II ACCMIP (years 1980–2010) and Lamarque et al. (2011) (years 2020–2100).

In 2007, the IPCC reported a range from -0.1 to -0.9 W m^{-2} for the aerosol direct forcing and from -0.3 to -1.8 W m^{-2} for the indirect forcing (excluding indirect effects beyond the cloud albedo effect). The magnitude estimate of the direct effect has since decreased, ranging from -0.05 to -0.31 W m^{-2} (Kulmala et al., 2011). Isaksen et al. (2009) found cloud albedo forcings in the literature ranging from -0.3 to -1.4 W m^{-2}. Cloud albedo forcing of -0.83 W m^{-2} was found for the year 2010 in Skeie et al. (2011). Recent estimate of the total aerosol forcing (direct+indirect effects) of year 2010, derived from observations of radiation imbalance and ocean heat uptake, was

-1.6 W m^{-2} (Hansen et al., 2011), identical to the one found in **Paper II**.

The predicted future reductions in emissions of aerosols and their precursors, as described in Sect. 6.2, can lead to a significant loss in aerosol cooling (Arneth et al., 2009, **Papers II and III)**. With continuingly increasing warming from GHGs, it has been suggested if either some aerosol emissions should not be decreased (e.g. sulfur emissions from shipping over remote oceans) or if aerosols should be deliberately injected to either troposphere or stratosphere. The issue of geoengineering by aerosols has been around for decades, and the research continues to search for applicable, efficient and safe frameworks.

7 Review of papers and the author's contribution

Figure 8 summarizes the processes studied in this thesis. I am solely responsible for writing the introductory part of this thesis.

Paper I studies the effect of new particle formation and biogenic SOA formation on aerosol and cloud droplet number concentrations. A semi-empirical parameterization for nucleation is included in the ECHAM5-HAM, showing that nucleation can have a significant contribution to cloud droplet concentration. A kinetic model is introduced for the condensation of organic vapours. I am responsible for the model development and simulations, data analysis, and wrote a major part of the paper.

Paper II studies the role of new particle formation on aerosol concentrations in the years 1750, 2000 and 2100. The paper shows that including nucleation in the model increases the present-day anthropogenic aerosol forcing. More importantly, a strong decrease is seen in the aerosol forcing by the year 2100, due to reductions in both primary aerosol and SO_2 emissions. Two potential climate feedbacks (DMS and BVOC) are studied. I am responsible for the model simulations, data analysis, and for writing most of the paper.

Paper III investigates the role of organic vapours on aerosol formation and growth in more detail. Two BVOC emission datasets and five nucleation mechanisms are applied in ECHAM5.5-HAM2. Including organic vapours in the nucleation parameterization is shown to improve present-day number concentrations compared to observations. It is shown that increasing future BVOC emissions can provide more CCN, compared to CO_2 inhibited BVOC emissions. I am responsible for the model simulations, data analysis, and writing the paper.

Paper IV shows the global effect of nitric acid on cloud droplet activation. It is shown that present-day nitric acid concentrations can have a strong increase in the modeled cloud droplet concentrations, leading to an increase in aerosol indirect effect. It is also shown that the decreasing future aerosol concentrations might lead to enhanced indirect effect from nitric acid. I am responsible for the model simulations, data analysis, and for writing most of the paper.

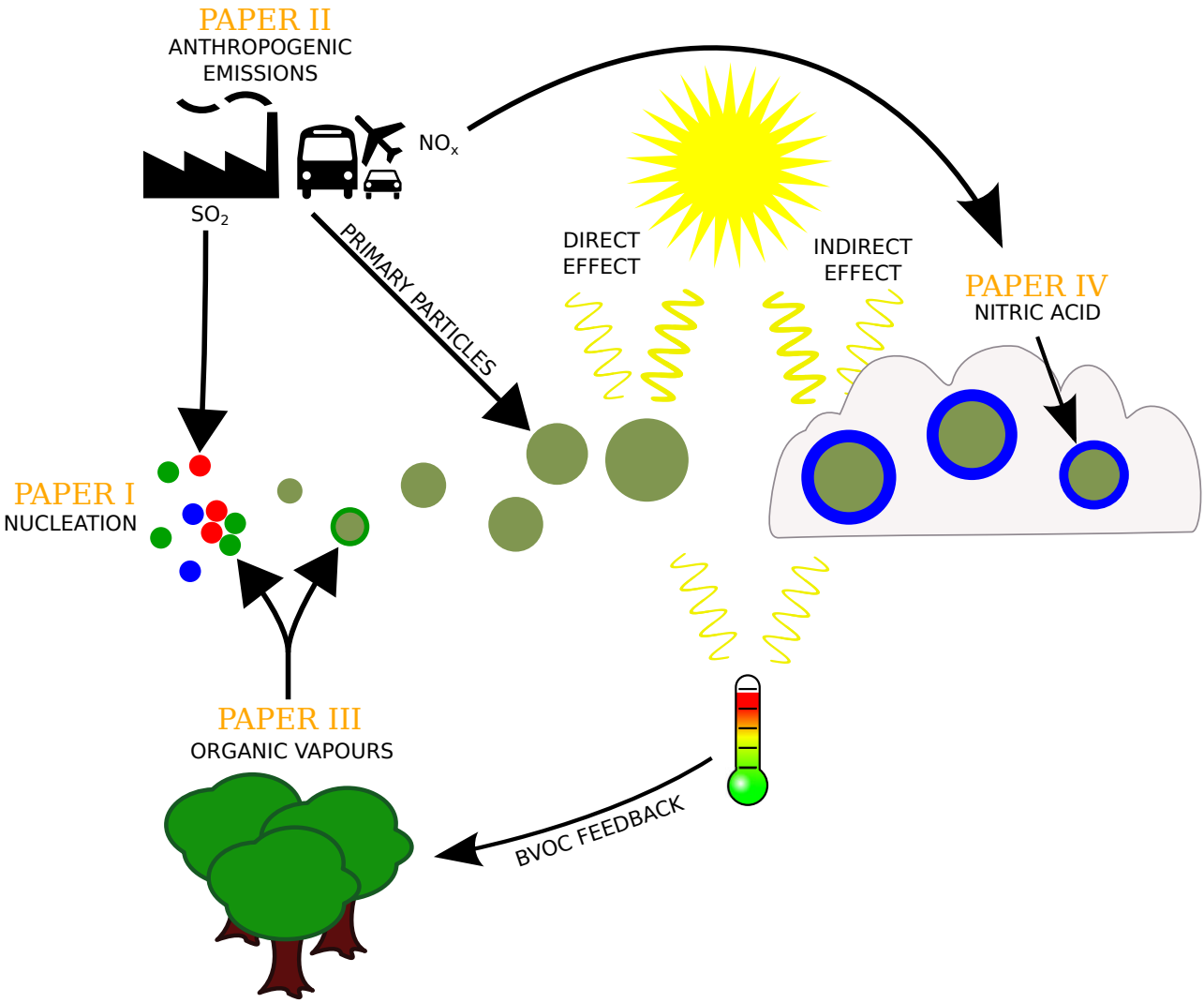

Figure 8: Simplified schematic of the processes studied in this thesis, indicating the main focus of each paper.

8 Conclusions

The main focus of this work has been atmospheric new particle formation. Parameterizations of boundary layer nucleation based on atmospheric observations have been included in the global climate model ECHAM5-HAM, leading to improvements in the modeled aerosol concentrations (**Papers I and III**). It was also found that nucleation, occurring both in boundary layer and free troposphere, has a significant impact on cloud properties due to increases in cloud droplet number concentrations. While the

indirect effect due to new particle formation is strong in the present-day conditions, it was shown in **Paper II** that the large reductions in anthropogenic SO_2 emissions by the year 2100 would act to diminish new particle formation, leading to a drastic decrease in the total aerosol forcing.

Atmospheric observations indicate that the growth of newly formed particles is largely due to organic vapours. To establish the connection between biogenic VOCs and nucleation, the description of secondary organic aerosols in ECHAM5-HAM was reformulated in **Paper I**. The improved model was then used in **Paper II** to show that a future increase in BVOC emissions could provide more growth for nucleated particles, leading to additional cooling. The role of BVOCs on climate was further investigated in **Paper III**, where also the role of organic vapours in nucleation was included. It can be concluded that increased future BVOC emissions lead to increased CCN concentrations, potentially creating a negative climate-feedback. However, the magnitude of the climatic effect is complicated by simultaneous changes in cloudiness.

It was shown in **Paper IV** that including nitric acid in ECHAM5-HAM has a significant effect on cloud droplet concentrations and on the indirect aerosol effect. Since the future reductions of NO_x emissions are expected to be more subtle than those of SO_2, the increased cloud droplet activation due to nitric acid could hinder the warming seen in **Papers II and III**.

Firstly, this thesis investigates processes that lead the path from molecular scale to changes in cloud properties: nucleation of new particles from sulfuric acid and organic vapours, growth of these particles to CCN sizes by organics, and finally the enhanced cloud droplet activation due to condensing nitric acid. Secondly, it is shown that these processes make a strong present-day aerosol forcing. Thirdly, the potential future evolution of the aerosol-climate interaction is studied with several combinations of processes and emission scenarios. In summary, it can be concluded that the anthropogenic aerosol forcing is decreasing, even to a large extent, by the year 2100. This decrease can be counteracted so some extent by natural climate feedbacks.

Although this thesis provides quantifications of several aerosol-climate effects, future developments in theoretical, computational and observational frameworks are essential to further constrain these effects. The increasing computing power will allow for more detailed description of aerosol properties and relevant chemical and microphysical processes, as well as finer spatial resolutions. Evaluation of simulated aerosol number

concentrations is still limited by the poor coverage of long-term observations, especially over the remote continental and marine regions, and over the Southern Hemisphere.

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